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Synergy of Inorganic Fillers in Composite Thermoplastic Polymer/ Ionic Liquid/LiTFSI Electrolytes

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The development of novel solid electrolytes, which can be processed using solvent-free methods, is one of the keys for successful industrialization of solid state batteries and their further implementation in electrical vehicles. Here, we study thermoplastic solid state electrolytes based on polyethylene oxide (PEO), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and two inorganic fillers with different morphology and nature (modified sepiolite (TPGS-S) and garnet-type Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ (LLZNO) prepared by solvent free extrusion method. Several thermoplastic polymer electrolytes (TPEs) are prepared and comprehensively studied. Composite thermoplastic electrolyte TPE-S10G10 containing 10 wt% of TPGS-S and 10 wt% of LLZNO fillers shows the best electrochemical performance in Li-LiFePO₄ solid state batteries operating under 0.2C/0.5D cycling conditions at 60 °C. Solid state cell with TPE-S10G10 can be exploited during the development of TPEs, is clearly demonstrated.

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Climate change due to global warming and air pollution is a very serious challenge for the sustainable future of the planet and human civilization.¹ As part of various global measures, European Commission has set mandatory the EU average fleet-wide emission reduction for new cars as 95 g_{CO2} ·km⁻¹ by 2021.² Obviously, such ambitious goal cannot be achieved without partial or complete electrification of the new car fleet. As a consequence, the automotive industry is looking for high energy, robust, safe, relatively cheap and easily recyclable batteries for the new generation of cars.

In this context, lithium metal batteries are considered as one of the most promising candidates to fulfill the vacant spot.^{3,4} However, lithium metal anode possesses significant electrochemical and safety related limitations to be directly used in contact with liquid electrolytes. On the other hand, mechanically and thermally stable solid electrolytes can be considered as a feasible way to enable the employment of lithium metal anode.

Composite electrolytes have attracted a lot of attention as a promising class of solid electrolytes to tackle the intrinsic problems associated with each constituent, typically polymer electrolyte and inorganic compound.^{5–9} By integrating all merits of the individuals, the disadvantages of one constituent are compensated by the advantages of the other; hence the physicochemical and electrochemical properties of the composite electrolytes can be enhanced. The association of polymer matrix and inorganic constituents mostly leads to complementary effects on the lithium ion conduction of composite electrolytes.^{10–15} The most studied composite electrolytes are combining polyethylene oxide (PEO)-based polymer electrolytes and inorganic fillers. PEO represents the most employed polymer in solid polymer electrolytes (SPEs) due to its ability to solvate high concentration of lithium salt even at room temperature.¹⁶ Being a semi-crystalline polymer, ion conduction is possible only in the molten state, where PEO is a viscous liquid.¹⁷ PEO-based electrolytes possess good adhesion and flexibility but poor mechanical properties and narrow electrochemical stability window at 60-80 °C; moreover, they generally have low ionic conductivity $(\sim 10^{-5} \text{ S} \cdot \text{cm}^{-1})$ below melting point.^{18,19}

Modified PEO-based solid electrolytes have been developed to reduce the crystallinity degree and melting temperature while maintaining good mechanical properties. These electrolytes are composed by a conductive matrix, lithium salt and different kinds of additives, such as low molecular weight compounds (liquids) or/and inorganic fillers. In current research, liquid phases are typically room temperature ionic liquids,²⁰ replacing the commonly used cyclic carbonates or low molecular weight polyethylene glycol. Inorganic fillers comprise both inert (non-conductive) and Li-ion conductive ceramic fillers. Non-conductive inorganic fillers are nano- or micro-sized particles added in order to improve mechanical resistance, and also to hinder the supramolecular arrangement of polymer chains, thus preventing the crystallization.^{9,21–23} Among the reported fillers, SiO_2 ,^{24,25} TiO_2 ,²⁴ and $Al_2O_3^{25-27}$ are the most investigated ones. Several studies^{24,27} demonstrated that a maximum of 10 wt% of nonconductive inorganic filler can be successfully dispersed in a continuous medium in order to maintain a homogeneous distribution avoiding the presence of larger aggregates. Despite being highly effective in the improvement of physical and electrochemical properties of SPEs, nano-sized fillers suffer a major limitation. Indeed, they tend to macro-phase separate forming aggregates that can hinder Li⁺ ion transport, hence decreasing ionic conductivity.²⁷ The most common solution to overcome such an issue is surface functionalization of nanoparticles with organic molecules in order to increase the colloidal stability of the mixture.²⁵

Conductive inorganic fillers are generally high conducting solid inorganic electrolytes (SIEs) dispersed in a polymer matrix to not only improve mechanical resistance but also the electrochemical performance.^{29–32} They are promising materials for the development of solid-state lithium batteries with high Li-ion conductivity and transference number close to unity. Generally, solid-state electrolytes with lithium ionic conductivity in the order of 10^{-4} S·cm⁻¹ at room temperature are suitable for solid-state battery (SSB) applications. Among them, garnet-type electrolytes have currently attracted much attention due to their high ionic conductivity reaching 10^{-3} S·cm⁻¹ at room temperature, ^{33–35} excellent chemical stability vs lithium metal and wide electrochemical window (up to 6 V) compared to other solid-state inorganic electrolytes.^{36,37} Li₇La₃Zr₂O₁₂ (LLZO) solid electrolyte with the known garnet structure Li₅La₃Nb₂O₁₂ has been

widely studied due to its high ionic conductivity of about $2 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at room temperature and activation energy (E_a) of 0.30 eV.³² LLZO garnet material can be crystallized into two polymorphs: tetragonal symmetry (space group I41/acd, No. 142) and cubic symmetry (space group Ia-3 d, No. 230). It is generally desired to stabilize the cubic phase, as its ionic conductivity is about two orders of magnitude higher than that of the tetragonal phase $(10^{-4} \,\mathrm{S \cdot cm^{-1} \, vs} \, 10^{-6} \,\mathrm{S \cdot cm^{-1} \, at RT})$, and its activation energy for ion conduction is nearly twice lower ($\sim 0.30 \text{ eV}$ vs $\sim 0.54 \text{ eV}$ of tetragonal phase).^{34,38,39} Aliovalent doping of LLZO via Nb or Ta substitution on the Zr site helps to stabilize the cubic structure and further increase ionic conductivity of LLZO garnets.^{33,35–37} Despite their high ionic conductivity with transference number close to unity, SIEs in general and particularly garnet-structured electrolytes are hard and fragile ceramics, consequently difficult to integrate into a solid-state battery and further scale-up. To merge good features of both ceramic and polymeric electrolytes, a promising approach is to disperse Li-ion conducting ceramic electrolytes into a polymer matrix in order to obtain flexible thermoplastic solid electrolytes (TPEs). In principle, the addition of Li-ion conductive inorganic filler, e.g. LLZO garnet, should produce several improvements in the physicochemical and electrochemical properties of composite electrolytes: i) increase the ionic conductivity due to high lithium ion content and possible decrease of the crystallinity of polymer matrix; ii) increase Li-ion transference number; iii) enhance interfacial stability, mechanical and thermal stability for safety improvement.8,29-32,40

It is important to note that successful development and further industrialization of solid state battery technology depend to a great extent on the development of novel solid electrolyte materials which can be effectively processed using environmentally friendly methods (solvent free, aqueous etc.). Solvent-casting is a widely employed method for preparation of solid polymer electrolytes; however, the elimination of residual traces of organic solvent and moisture from the final composites can be an issue especially in the presence of ceramics that can coordinate water solvent's molecules on their surface. These traces may react with lithium metal, leading to an increase in Li/solid electrolyte interfacial resistance, which is detrimental to cycling performance at cell level. In addition, the use of excessive amount of volatile and toxic organic solvents required for solvent-casting method will definitely raise the price of final solid state battery.

In contrast, solvent-free processing, e.g. extrusion or hotpressing, completely overcomes such issues since it does not require solvents during the whole process.^{32,41–46} Moreover, with this method, reproducibility is much better, the duration of electrolyte preparation is significantly reduced and industrial scaling is simplified. Compared to solvent-casting process, composite electrolytes prepared by a sustainable and solvent-free method show better compatibility with Li metal anode, and consequently improved cycling performance, as demonstrated in our previous work.⁴¹

To the best of our knowledge, usually the development of composite electrolytes turns upon optimization of content, size, and surface properties of certain inorganic filler whereas mixtures of fillers is yet quite an unexplored area. Therefore, in this context, we present the results of the development of novel composite thermoplastic polymer electrolytes (TPEs) based on a polyethylene oxide (PEO) matrix, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR₁₄TFSI) ionic liquid and two types of inorganic fillers of different nature and morphology: surface modified sepiolite (TPGS-S) and lithium ion conductive Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ ceramic (LLZNO). TPGS-S behaves as a physical crosslinker and endows otherwise liquid electrolytes based on polyethylene oxide and ionic liquids with a solid character,^{43–46} while LLZNO improves the electrochemical performance of Li-LiFePO₄ solid state coin cells. All composite thermoplastic electrolytes have been prepared using solvent-free extrusion method and comprehensively characterized.

Experimental

Materials.—PEO with Mw of $5 \cdot 10^6$ g \cdot mol⁻¹ from Aldrich was used to prepare the composites. LiTFSI, from Aldrich was dried under vacuum for 24 h. The 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI) of 99.9% purity employed to prepare the electrolytes was purchased from Solvionic and used as received. Neat sepiolite, kindly supplied by TOLSA S.A., was dried under vacuum for 24 h. D- α -tocopherol polyethylene glycol 1000 succinate (TPGS), used to prepare the modified sepiolite TPGS-S, was purchased from Aldrich and used as received. Details on the simple and relatively cheap preparation process of TPGS-S have appeared elsewhere.⁴⁷ Lithium ion conductive Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ (LLZNO) garnet ceramic was synthesized by low temperature solid state reaction via planetary ball milling (Retsch PM100). This composition was rationally selected due to its highest ionic con-ductivity, as reported earlier.³³ The raw materials were stored in dry room condition and used as received. Stoichiometric amounts of LiOH·H₂O (99.95%, Aldrich), La₂O₃ (99.99%, Aldrich), ZrO₂ (<100 nm particle size, Aldrich), Nb₂O₅ (99.99%, Aldrich) were first weighed, and then sealed in tungsten carbide (WC) jar with WC balls under dry room condition (dew point below -50 °C). The mixture was subsequently transferred to outside and mechanically ball-milled under atmospheric condition for 16 h in isopropanol. 10 wt% excess of LiOH·H2O precursor was added to account for lithium evaporation during heat treatment at high temperature. The resulting mixture was calcined at relatively low temperature 900 °C for 12 h in air, and subsequently ball-milled for another 3 h in isopropanol to obtain the submicron-sized garnet powder (Fig. S1a is available on-line at stacks.jop.org/JES/167/070519/mmedia). The final powder was then heat-treated at 700 °C for 4 h in air to completely remove solvent traces and/or contamination, and quickly transferred to dry room for storage and later usage. High ionic conductivity of synthesized Li7La3Zr1.75Nb0.25O12 garnet was confirmed by electrochemical impedance measurements (see Fig. S1b).

Preparation of thermoplastic solid electrolytes.—Electrolytes' compositions are shown in Table I. The components were meltcompounded in a Haake MiniLab extruder at 80 rpm, at 160 °C and for 20 min. According to the previous work,⁴⁴ these conditions lead to adequate mixing of the components while ensuring no PEO degradation. The components were manually premixed before adding to the extruder. Table I includes PEO-LiTFSI and TPE-S2.5 electrolytes studied in the former work for comparison.⁴¹

It may seem surprising that wt%, instead of vol%, have been kept the same when formulating the electrolytes with both fillers. LLZNO garnet has a theoretical density of 5.14 g·cm⁻³, which is more than two-fold higher than that of TPGS-S ($\approx 2.2 \text{ g·cm}^{-3}$). TPE-S10 contains about 7 vol% of TPGS-S; to prepare a similar vol% of LLZNO, more than 20 wt% of LLZNO should have been added to the electrolyte, which is not feasible. Hence we have kept the same wt% for both fillers.

Physicochemical characterization of thermoplastic solid electrolytes.—Characterization of electrolytes was conducted on films with controlled thickness (\sim 500 μ m for electrochemical measurements and \sim 1000 μ m for rheological measurements), processed by compression molding at 75 °C during 3 min.

Scanning electron microscopy (SEM) was performed using a Hitachi SU-8000 instrument. Samples were fractured after immersion in liquid nitrogen and the sections were observed unmetalized. To visualize both TPGS-S and garnet distribution in electrolyte TPE-S10G10, energy dispersive X-ray spectroscopy (EDX) mapping of Si (TPGS-S), La and Zr (LLZNO) was employed.

Atomic Force Microscopy (AFM) of the electrolytes were carried out on the surface of the electrolyte films using a Veeco Multimode scanning probe microscope equipped with a Nanoscope IV, and a

Solid electrolyte	PYR ₁₄ TFSI, mol L ⁻¹	LiTFSI, mol L^{-1}	PEO, mol L^{-1}	PEO/LiTFSI, molar ratio	TPGS-S, wt%	LLZNO, wt%	Fillers, ∑wt%	Fillers, ∑vol%
PEO-LiTFSI	_	0.89	20.7	20	_	_	_	_
TPE-S2.5	1.55	0.78	9.66	12	2.5	_	2.5	1.7
TPE-S10	0.52	1.20	14.34	12	10	_	10	6.6
TPE-S20	0.68	1.01	12.11	12	20	_	20	13.9
TPE-G10	0.54	1.24	14.93	12	_	10	10	2.8
TPE-G20	0.74	1.10	13.20	12	_	20	20	6.1
TPE-S10G10	0.72	1.07	12.87	12	10	10	20	8.4

Table I. Formulations of	f the	composite	thermoplastic	electrolytes.
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controller operating in tapping mode with a phosphorus-doped silicon cantilever (RTESP model).

Differential scanning calorimetry (DSC) was performed through heating/cooling/heating cycles from -80 °C to 120 °C at the heating rate of 10 °C·min⁻¹; thermograms and data reported in this work refer to the second heating cycle. The crystallinity percentage (X_c) was determined as in previous work.⁴¹

Attenuated total reflection—Fourier-transform infrared spectroscopy (ATR-FTIR) spectra of all electrolytes were obtained using FTIR Perkin-Elmer Spectrum-Two with 10 scans and resolution of 4 cm^{-1} . The method was employed to check if the actual composition of the composites was in agreement with the nominal one, and if it was uniform throughout the membrane. The absence of significant degradation levels was also inspected.

Rheological measurements were conducted using an Advance Rheometer ARG2 with a 20 mm steel plate. Prior to the launching of the experiment, samples were annealed in the rheometer for 10 min at the extrusion temperature (120 °C) and then stabilized at 75 °C for 5 min. Oscillatory frequency sweeps were measured in the frequency range of 500–0.01 rad·s⁻¹ using a stress amplitude of 10 Pa, which lies within the linear viscoelastic regime for the tested samples. Three measurements on each electrolyte were done. The average of the elastic shear modulus G' at 0.05 rad·s⁻¹ and its standard deviation are shown below, together with the crossover frequency of G' and the viscous shear modulus G''. Below the crossover frequency G'' > G', the material must be then considered a liquid.

Ionic conductivity (σ) was determined using a NOVOCONTROL GmbH Concept 40 broadband dielectric spectrometer (Novocontrol Technologies GmbH, Montabaur, Germany) in the temperature range from -50 °C to 90 °C and in the frequency range between 0.1 Hz and 10⁷ Hz. Disk films of 2 cm diameter and ~500 μ m thickness were inserted between two gold-plated flat electrodes, subsequently a frequency sweep test was performed every 10 °C, cooling to -50 °C and then heating to 90 °C; after that, the same measurements were performed by cooling from 85 °C to 25 °C. Values of σ were calculated using conventional methods based on Nyquist plot and phase angle as a function of frequency plot.

Electrochemical characterization of thermoplastic solid electrolytes.—Lithium ion transference number (t_{Li+}) of the prepared solid electrolytes was measured at 60 °C by Bruce-Vincent-Watanabe method using combined alternating current (AC) impedance and direct current (DC) polarization (more details can be found in Ref. 41).

Electrochemical performance of the developed solid electrolytes was studied in Li/TPE/LiFePO₄ solid state coin cells at 60 °C. Battery grade 50 μ m thick lithium foil received from Albemarle was used as the negative electrode. Composite positive electrode was prepared using 75 wt% of carbon coated LiFePO₄ material (D50: $2-4 \mu m$), 5 wt% of carbon black C-ENERGY Super C45 (IMERYS Carbon & Graphite) as a conductive additive, 20 wt% PEO-LiTFSI solid electrolyte (EO/Li~20) as a binder with lithium ion conductivity. Homogenous cathodic slurry was prepared in acetonitrile media using DISPERMAT[®] LC30 mixer and then was casted onto carbon coated aluminum current collector with low interfacial resistance and improved corrosion stability. The target loading of positive electrode was set as $0.5 \text{ mAh} \cdot \text{cm}^{-2}$. The solid electrolytes in Table I were prepared in the form of membranes by hot-pressing at 75 °C with a pressure of 2 Ton during 3 min using a Specac[®] hot press.

Three layered sandwich-like structure consisting of positive electrode, solid electrolyte and Li metal anode was laminated and sealed in 2025 coin cell case using Hohsen crimper. Before cycling, assembled coin cells were kept for 3 h at 60 °C to enhance internal contact between solid electrolyte and electrodes. Finally, solid state coin cells were cycled at 60 °C within the 2.5–3.8 V cycling voltage range using BaSyTec cell test system.

Results and Discussion

Physicochemical characterization of thermoplastic solid electrolytes .-- The electrolytes studied in this work are highly fillerloaded. SEM images of TPE-S2.5, TPE-S10, TPE-S20, and TPE-S10G10 thermoplastic solid electrolytes suggest a good distribution of TPGS-S fibers in the electrolyte bulk (Fig. 1, on the left). Nonetheless, due to the excellent filler/matrix compatibility, it is difficult to distinguish each component as well as to interpret the imaging data. AFM analysis allows a better characterization of filler state and distribution through phase and amplitude images (Fig. 1, in the middle and on the right). The surface of all the studied electrolytes shows well dispersed and isolated fibers of TPGS-S, which are homogeneously distributed, in all electrolytes. As expected, TPE-S2.5 contains fewer fibers than TPE-S10, and TPE-S20. On the contrary, in terms of superficial fiber concentration, there is no distinct difference between TPE-S10 and TPE-S20. Comparison of these three electrolytes indicates that the concentration of TPGS-S fibers on the surface is not directly proportional to the concentration of fibers in the bulk, which is not surprising as surface morphology is known to depend not only on composition but also on cooling conditions. On its turn, the AFM of TPE-S10G10 shows abundant TPGS-S on the surface, but a lower concentration than TPE-S10.

Figure 2 shows the EDX mapping on SEM images of TPE-S10G10 using Si to track TPGS-S, La and Zr to track garnet type filler. It can be seen that TPGS-S is well dispersed in the form of small aggregates and probably isolated fibers, and that some large aggregates also exist. LLZNO ceramic is in the form of micrometric spherical particles, relatively well distributed throughout the sample.

Table II summarizes physicochemical and electrochemical data of the electrolytes regarding the thermal stability, phase transition and relaxation, rheological behavior and ionic conductivity at 25 °C. T₅, the temperature at 5 wt% loss in TGA analysis, is well over 300 °C in all the investigated electrolytes, which can therefore be considered thermally stable. Crystallinity studied by DSC is not significant, as it is very low (<5 wt% in all cases), and T_m is around room temperature. The high concentration of LiTFSI and the large ratio of inorganic fillers suppress the crystallization of PEO in the electrolytes. The glass transition (T_g) of PEO is clearly detectable in all the electrolytes, as illustrated in Fig. S2. TPE-S10, TPE-S20, TPE-G10, TPE-G20 and TPE-S10G10 have very similar T_g at about -50 °C, about 8 °C higher than that of TPE-S2.5. This suggests T_g is mostly governed by the content of LiTFSI, BMPTFSI, and PEO, and very little by the amount and nature of the filler.

All the new electrolytes studied in this work are very similar among them as regards thermal stability, crystallinity, melting point and glass transition. This simplifies the comparison of their rheological and electrical properties. It has also been found that filler dispersion is good and comparable between electrolytes, and that the concentration of TPGS-S on the surface is not proportional to its nominal concentration.

Rheology has been studied to discriminate between solid-like and liquid electrolytes at 75 °C. The average of at least three different measurements of the elastic shear modulus G' at 0.05 rad s^{-1} is shown in Table II, together with the crossover frequency, and Fig. S3 includes the frequency sweeps. The crossover frequency is not detectable in TPE-S10, TPE-S20 and TPE-S10G10, meaning that only these three electrolytes can be considered as solid-like in the investigated temperature range, even if the solid components are only TPGS-S, and LLZNO (in case of TPE-S10G10). On the contrary, TPE-G10 and TPE-G20 behave as viscous liquids at 75 °C. Increasing TPGS-S amount from 2.5 wt% (TPE-S2.5) to 10 wt% (TPE-S10) rises the elastic modulus of the electrolyte from G'0.05 rad s⁻¹ \approx 14 kPa to \approx 50 kPa, which is in the range of elastomeric materials. Addition of TPGS-S up to 20 wt% of TPGS-S (TPE-S20) produces no further increase in the modulus, which is as expected since 10 wt% is already a very large amount of filler.



Figure 1. SEM (x10,000) (left) and AFM phase (middle) and amplitude (right) images of the TPGS-S containing thermoplastic electrolytes.

By substituting TPGS-S for LLZNO, TPE-G10 electrolyte with 10 wt% of garnet behaves as a very viscous liquid at 75 °C, with a crossover ω =0.05 rad·s⁻¹ and a G'≈8 kPa. When garnet content is increased to 20 wt%, the crossover frequency increases to 1.26 rad·s⁻¹ and G'≈1 kPa, i.e. the viscosity of the liquid decreases, suggesting that there is not an attractive interaction between polymer electrolyte and garnet, and that the presence of high amount of the ceramic releases entanglements and makes the material less viscous.

The rheology of TPE-G10 and TPE-G20 clearly demonstrates that TPGS-S is necessary to produce a solid thermoplastic electrolyte even if garnet filler is added. Hence, TPE-S10G10 was prepared, combining 10 wt% TPGS-S with 10 wt% LLZNO garnet ceramic. Regarding the rheological data this electrolyte is very similar to TPE-S10, which also contains 10 wt% of TPGS-S (Table II).

Long term stability experiments were carried out to check whether the electrolytes are structurally stable for a long period of time. As shown in Fig. S4, the electrolytes without TPGS-S slowly evolve to a macroscopic phase separation and behave as viscous liquids, while those containing TPGS-S are structurally stable for a period of years and can be hot pressed into thin, manageable membranes. As mentioned above, these membranes have elastic modulus \approx 50 kPa at 75 °C, which anticipates moderation of lithium dendritic growth.

Moreover, we have demonstrated excellent shapeability and easy handling of TPE-S20 in Video S1.

Ionic conductivity (σ).—Figure 3 shows σ values of all investigated electrolytes within interval of 0 °C–90 °C. No



Figure 2. SEM image (x250) of TPE-S10G10 (a) and EDX mapping of Si (b), Zr (c), and La (d) on this image.

step-like variations are observed, and σ on heating from -50 °C to 90 °C (solid symbols) is the same as σ on cooling (open symbols). Within that temperature range no melting (on heating) or crystallization (on cooling) is expected, as the crystallinity of these electrolytes is negligible. TPE-S2.5, which is included for comparison, shows the highest σ as expected due to its larger liquid fraction and lower filler content. In all the temperature range, σ varies in the order of TPE-S10G10 > TPE-G20 > TPE-S20 > TPE-G10 > TPE-S10. Actual values of $\sigma_{25^{\circ}C}$ and $\sigma_{60^{\circ}C}$ can be found in Table II. Though differences are small, TPE-S10G10 is more conductive in all the range.



Figure 3. Ionic conductivity (σ) of the investigated electrolytes as a function of temperature.

Only a slight increase in σ is seen in the electrolytes containing LLZNO garnet compared to those containing only TPGS-S. It has to be recalled that electrolytes with TPGS-S include volume fractions of the filler which are over 2-fold higher than those with the same wt % of LLZNO, and hence tortuosity is significantly higher in the former than that in the latter. In any case, no significant increase in overall conductivity can be expected, as conductivity of LLZNO at 60 °C ($\sigma_{60^\circ C}$) is about 0.6 mS·cm⁻¹ (Fig. S1b), which is lower than the total conductivity of the thermoplastic electrolyte in the absence of garnet (e.g., $\sigma_{60^\circ C} \approx 0.95$ mS·cm⁻¹ in case of TPE-S20).

Electrochemical properties of Li-LiFePO₄ solid state coin cells.—The electrochemical performance of Li-LiFePO₄ coin cells equipped with different solid electrolytes is depicted in Fig. 4. Previously, we have demonstrated that thermoplastic electrolyte (in this paper marked as TPE-S2.5) incorporating 2.5 wt% of TPGS-S significantly improves the cyclability of Li-LiFePO₄ solid state coin cells comparing to classical PEO-LiTFSI electrolyte.⁴¹

As seen in Fig. 4, increasing of TPGS-S content to 10 wt% (TPE-S10) has a positive impact on the electrochemical performance in terms of capacity retention and coulombic efficiency. When the content of TPGS-S is further increased to 20 wt% (TPE-S20), the discharge capacity decreases by 5%, however, the cells show better capacity retention in comparison with TPE-S10 (Fig. 5).

On the other hand, hybrid electrolytes TPE-G10 and TPE-G20 with 10 wt% and 20 wt% of lithium ion conductive ceramic LLZNO, respectively, demonstrate quite similar electrochemical performance in Li-LiFePO₄ cells. Nevertheless, the addition of higher amount of Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ filler causes some negative impact on the coulombic efficiency at the end of cycling.

The mixture of two fillers with different nature and morphology in the electrolyte TPE-S10G10 proves to be an excellent strategy to improve the electrochemical performance of the solid state battery.

		DSC (°C)			Rheology (75 °C)				
Solid electrolyte	T_5	T _m	Tg	X _{c,} %	$G'_{0.05}$ rad·s ⁻¹ , kPa	$\omega_{(G'=G'')}, rad \cdot s^{-1}$	$\sigma_{25 \ ^{\circ}\mathrm{C},} \mathrm{mS} \cdot \mathrm{cm}^{-1}$	$\sigma_{60 \ ^{\circ}\mathrm{C},} \mathrm{mS} \cdot \mathrm{cm}^{-1}$	$t_{Li+} \; (60 \; ^\circ C)$
PEO-LiTFSI	390	53	-38	32	(*)	(*)	0.01	0.50	0.25 ± 0.01
TPE-S2.5	376	37	-58	5	13.5 ± 6.4	0.01	0.51	3.03	0.08 ± 0.01
TPE-S10	356	32	-48	3	51.5 ± 22.5	not seen	0.10	0.91	0.10 ± 0.03
TPE-S20	336	34	-50	1	45.6 ± 7.5	not seen	0.13	0.95	0.26 ± 0.06
TPE-G10	362	34	-49	1	8.0 ± 5.3	0.05	0.15	1.19	0.05 ± 0.003
TPE-G20	351	_	-51		1.2 ± 0.9	1.3	0.18	1.22	0.06 ± 0.04
TPE-S10G10	358	23	-52	1	53.4 ± 15.7	not seen	0.19	1.45	0.04 ± 0.002

Table II. Physicochemical and electrical properties of the composite thermoplastic electrolytes.

Note: *-Rheology of PEO-LiTFSI could not be measured under the same conditions of TPEs (temperature, shear rate), probably, due to higher stiffness.



Figure 4. Electrochemical performance of solid-state coin cells Li-LiFePO₄ with the developed solid electrolytes: (a) specific discharge capacity, (b) discharge capacity retention, (c) coulombic efficiency vs cycle number, (d) cycle number at 80% of initial discharge capacity (*-PEO-LiTFSI based cell has failed having about 94% of initial discharge capacity). Cycling conditions: 60 °C, Constant Current-Constant Voltage (CCCV) charge at 0.2C (charge current cut off 0.1C), discharge at 0.5D, cycling interval 2.5–3.8 V, positive electrode loading 0.5 mAh·cm⁻².



Figure 5. Graphical abstract with initial discharge capacity values vs number of cycles of Li-LiFePO₄ cells with all tested TPEs (synergetic effect between TPGS-S and garnet is depicted with arrows).

Indeed, it demonstrates the best electrochemical performance with the highest initial discharge capacity and the longest cyclability of 540 cycles, with the most stable coulombic efficiency (Fig. 4 and Fig. 5). We believe that this behavior is possible due to the combination of the solid character provided by TPGS-S to the polymer based electrolyte and the likely behavior of garnet as a lithium ion conductor. As a result, TPGS-S allows for a self-standing solid electrolyte with remarkable wettability of the electrodes and very stable morphological structure, while garnet ceramic contributes to the active Li⁺ ions in the solid electrolyte for long cycling periods. Moreover, the fact that coin cells under pressure and without any additional separator except the composite solid electrolyte are able to effectively cycle more than 650 cycles (during more than 5.5 months) at 60 °C is a firm prove of the excellent mechanical stability of the developed solid electrolyte in real solid state battery environment during long time.

Finally, in the light of possible SSB mass production, we consider that TPE-S10G10 solid electrolyte composed by cheap components, relatively low content of LLZNO and TPGS-S filler prepared by using solvent-free melt compounding will not bring any additional cost nor processing difficulties during its scale up and mass production. On the opposite, melt-compounding is a wellknown processing aid at industrial level, because of its simplicity, reproducibility, low price and easy implementation. Thus, this work shows how to produce a solid electrolyte for a solid state battery with improved electrochemical properties by using a scalable and sustainable processing method, i.e. in a technologically feasible way.

Conclusions

The thermoplastic solid electrolytes based on PEO, PYR₁₄TFSI, LiTFSI, and two inorganic fillers with different morphology and nature (modified sepiolite nanofibers TPGS-S and garnet-type Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ submicron particles) have been prepared using a sustainable and cost efficient solvent-free extrusion method and comprehensively characterized.

To the best of our knowledge, for the first time synergetic effect of inert and conductive fillers in TPE-S10G10 solid composite electrolyte has been demonstrated with enhanced rheological and mechanical performance, ionic conductivity at operating temperature as well as the electrochemical performance in Li-LiFePO₄ cells. As such, using a mixture of inorganic fillers with different morphology and nature is an effective approach towards the development of advanced composite solid electrolytes.

Moreover, we believe that this study opens immense possibilities to blend different kinds of fillers with synergetic effect as an additional source of composite electrolyte improvement toward more advanced lithium metal solid state batteries.

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